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<p>(54) Title: REDUCING THE EFFECTS OF WATER VAPOR AND LIQUID WATER ON OPTICAL WAVEGUIDE SENSORS (OWS) AND OPTICAL WAVEGUIDE CHEMICAL SENSORS (OWCS)</p> <div data-bbox="357 1155 1218 1596"> </div> <p>(57) Abstract</p> <p>The effects of water are eliminated from an optical waveguide chemical sensor by applying a hydrophilic coating which creates a pseudo water jacket. The hydrophilic coating absorbs water so that the waveguide sees a constant refractive index. The hydrophilic coating can reach equilibrium conditions in a high relative humidity environment or can be pretreated by exposure to water in a low relative humidity environment. A variety of hydrophilic polymers can be used.</p>		

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REDUCING THE EFFECTS OF WATER VAPOR AND LIQUID WATER ON
OPTICAL WAVEGUIDE SENSORS (OWS) AND OPTICAL WAVEGUIDE
CHEMICAL SENSORS (OWCS)

BACKGROUND OF THE INVENTION

5 The invention relates generally to optical waveguide sensors, and more particularly to waterproofing the sensors.

Optical sensors, as a group, depend on light interaction with the analyte of interest or a by-product of the analyte of interest. Making the requisite measurement, therefore, requires that all changes in the light be attributed to the analyte and not to other extraneous factors.

One of the key contributors to changing light propagation through an optical sensor is water in both the vapor (relative humidity, RH) and liquid forms. This is because water, in either form, changes the "waveguiding" of the light. Light transmission through an optical waveguide (waveguide, channeled waveguide, single and multi-mode fiber optics and optical "chips") is a total reflection phenomenon (Figure 1).

If the refractive indices of air, the core and the clad are N_0 , N_1 and N_2 , respectively, then the angle, measured from the perpendicular, at which the light enters the clad, θ_c , is defined as

$$\theta_c = \sin^{-1} (N_2/N_1) \quad (1)$$

Light incident at angles less than θ_c will enter the clad and be lost while light incident at θ_c or greater will be reflected back into the core. The numerical aperture (NA) of the waveguide is dependent on the entrance angle of the

light, A_m , by the relationship

$$N_0 \sin A_m = NA = (N_1^2 - N_2^2)^{1/2} \quad (2)$$

Light incident at angles greater than A_m will not be input into the waveguide but will be reflected. In addition, for
5 light to propagate through the waveguide, it is required that $N_1 > N_2$.

In examining equation (2), it can be seen that N_0 plays an important role in light propagation. If N_0 is replaced by N_w , the refractive index of water ($N_0 \approx 1.00$, $N_w \approx 1.33$) or N_{wv} , the refractive index of water vapor (> 1.00 , < 1.33) (i.e., relative humidity), it can be seen that the
10 conditions will change considerably which in turn changes light propagating through the fiber.

$$N_{wv} \sin A_m = NA = (N_1^2 - N_2^2)^{1/2} \quad (3)$$

15 The light transmission is also affected by the thickness of the clad, i.e., if the clad is not sufficiently thick, then the medium surrounding the fiber (water, water vapor, gases) influences light propagation because it also acts as a clad, effectively changing N_2 .

20 In evanescent wave sensors (Figure 2) and other side-coated sensors (Figure 3), this is further complicated since the clad is removed and replaced by a sensor chemistry. Klainer, et al, discuss this in U.S. Patents 4,846,548; 4,929,049; 5,026,139; 5,165,139; 5,165,005 and
25 5,253,037. In either the evanescent or other side-coated designs, the thickness of the sensing chemistry is deliberately kept small (10-1,000 Å). This serves two purposes: (1) it makes it easy for the target species to completely penetrate the sensing chemistry, and (2) it
30 results in improved sensitivity because small concentrations of target species causes large changes in the sensing chemistry.

The requisite for thin chemical sensing films,

unfortunately, leaves the fiber core dependent on N_0 , N_w or N_{wv} . The light propagation through the fiber, therefore, is dependent on the surrounding medium and this effect is mitigated by the present invention.

5 U.S. Patent 5,109,442 to Klainer describes a technique for waterproofing sensors against liquid water. This technique depends on keeping the water away from the sensor using surface tension. It further utilizes thick protective films ($>1,000 \text{ \AA}$) so that light transmission is
10 not affected by the surrounding medium. The latter is possible because the coating is put onto the sensor in a geometric pattern with spacers which allows the analyte to reach the sensing chemistry.

The scheme of U.S. Patent 5,109,442 does not work
15 for gases and vapors (including water vapor) because: (1) Liquid water is a large molecule due to the formation of hydrogen bonds giving the general formula $(H_2O)_n$, whereas water vapor is a single molecule $(H_2O)_1$; (2) Gases and vapors have no surface tension, and therefore, will pass through
20 the patterns as described in U.S. Patent 5,109,442; and (3) Gases and vapors have smaller molecular sizes than the species of interest so that excluding the gases and vapors would make it impossible for the larger target species to interact with the sensing chemistry. Water vapor, i.e.,
25 relative humidity, therefore, becomes a major concern both in detection and quantification because there is no quantitative way of determining which portion of light comes from the effect of water vapor on "waveguiding" and what part of the signal comes from the sensing chemistry.

30 The sides of the fiber, for all practical purposes, cannot be used for chemical sensing because the light does not reach the outer surface of the clad, or, in cases where the clad is removed, the light comes out the sides and cannot be collected effectively. However, when
35 the sensing reagents (N_3) are coated on the side of a fiber optic, whose clad (N_2) has been removed, a measurable effect occurs in the evanescent wave region (Figure 2). This effect can be used to identify and quantify a particular

species. The problem is that the evanescent wave does not penetrate very deep into the clad. This is a function of the thickness of the sensing material, the angle of the incident light, the wavelength of the light, and the refractive indices N_1 and N_3 . Proper selection of these parameters should assure that light is optimally transmitted through the fiber provided N_w or N_{ww} are not influential. In an evanescent wave sensor, the light penetration depth into the sensing chemistry is on the order of $1/4$ of the wavelength of the exciting light and this limits the allowable thickness of the reactive surface because only the depth to which the light penetrates can be interrogated, and any additional thickness represents an unacceptable threshold. Under these conditions, N_w or N_{ww} would be a deterrent.

Coating the sides of the fiber with sensing reagents can be very effective if all of the sensing chemistry can interact or react with the target species and if the resultant changes in light characteristics can be measured. The technique is accomplished by making a multilayered FOCS in which the reacting chemistry is "sandwiched" between the core and the clad (Figure 3), U.S. Patent No. 4,846,548. The approach is to make the refractive index, N_3 , of the reacting medium greater than N_1 and N_2 while keeping N_1 greater than N_2 . Thus, because N_3 is greater than N_1 , the light passes through N_3 and is sent back to the core when it reaches N_2 . Because N_1 is also of smaller refractive index than N_3 , it, too, acts as a clad and redirects the light through N_3 to N_2 . This reaction occurs over the length of the waveguide. Any reactions or interactions that do occur in the reactive layer are enhanced, because the light passes through the sensing medium many times, enhancing the signal response and making it much greater than with a tip-coated or evanescent wave FOCS. In this case, the output of the waveguide is a light annulus, dark in the center and with a bright ring.

It is essential that the clad, in addition to having the proper N_2 , be sufficiently porous so that the

species to be monitored has adequate access to the sensor chemistry. Clads that have a controlled pore size can also be used as protective or gas-permeable membranes. By covalently immobilizing the reactants to the core, any
5 chance of losing the sensing material by "leakage" through the porous polymer clad is obviated. In a similar manner, the clad/membrane is most effective when it is immobilized to the sensing chemistry. Its feasibility is demonstrated in U.S. Patent 4,846,548. It should be noted that this
10 sensor design is amenable to a variety of optical and spectrophotometric measurements. However, the sensor is susceptible to the effects of water.

SUMMARY OF THE INVENTION

According to one aspect of the invention, there is
15 provided an optical waveguide chemical sensor for detecting an analyte, comprising: an optical waveguide of refractive index N_1 ; a sensing chemistry of refractive index N_2 on the waveguide; a hydrophilic coating of refractive index N_2 on the sensor which maintains the sensor in a substantially
20 constant water environment.

According to another aspect of the invention, there is provided a method of eliminating the effects of exposure to water on an optical waveguide chemical sensor, comprising applying a hydrophilic coating to the sensor to
25 maintain a substantially constant water environment around the sensor.

The invention is method and means for eliminating the effects of water from an optical waveguide chemical sensor by applying a hydrophilic coating which preferably
30 creates a pseudo water jacket. The hydrophilic coating may absorb water so that the waveguide sees a constant refractive index. The hydrophilic coating can reach equilibrium conditions in a high relative humidity environment or can be pretreated by exposure to water before
35 use in a low relative humidity environment. A variety of hydrophilic polymers can be used.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-section of an optical fiber.

Fig. 2 is a cross-section of an evanescent wave sensor.

5 Fig. 3 is a cross-section of a side-coated sandwich type sensor.

Figs. 4a-g are cross-sections of waveguide chemical sensors with hydrophilic coatings.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

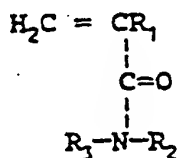
10 The basic principle of the invention is to put the optical sensor or optical chemical sensor into a situation where it always behaves as if it is in water, i.e., surround the optical waveguide and/or sensing chemistry with a pseudo "water jacket" so that light transmission is essentially the
15 same with and without water vapor present. This water jacket serves the purpose of making $N_0 = N_w = N_{ww}$ as discussed above.

The water jacket of the invention is formed of a hydrophilic material. In conditions where RH is high, e.g.,
20 in a well, it is relatively easy to maintain since equilibrium conditions will keep the hydrophilic material saturated. In low RH environments, however, it will be more difficult to maintain the water jacket since over time water will be lost to the environment. In those cases, the sensor
25 should be pretreated (e.g., dipped in water until equilibrium is reached) and then used for a time period that the coating maintains substantial water content.

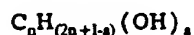
In application, the water jacket is made from a hydrophilic material(s) which attracts water and retains it
30 in the vicinity of the waveguide. This hydrophilic coating can be a polymer, inorganic or organic compound and even a "free" metal such as lithium (Li). This approach, however, can make it difficult for hydrophobic or ionic species to reach the sensing chemistry. In these cases, a percentage
35 of hydrophobic or ionic material is incorporated into the hydrophilic matrix to facilitate the transport of the species of interest into the sensing chemistry. In the same

vein, since water is now a desired molecule, pore size can be increased for better chemical transport. Listed below are examples of the types of hydrophilic compounds that can be used.

- 5 1. Poly(acrylamide), hydrolyzed to different degrees and crosslinked, alkali metal and alkaline earth metal salts of such polymer
2. Poly(hydroxy methacrylate)
3. Poly(hydroxy ethacrylate)
- 10 4. Poly(vinyl acetate) hydrolyzed to different degrees and crosslinked
5. Poly(acrylic acid), crosslinked
6. Poly(styrene sulfonic acid) and salts
7. Poly(vinyl alcohol) crosslinked
- 15 8. Partially carboxylated methyl cellulose
9. Partially esterified cellulose; methyl, ethyl, butyl esters of cellulose
10. Cellulose
11. Poly(n-acrylamidomethyltrimethyl) ammonium chloride
- 20 12. Poly(acrylic acid-co-styrene)
13. Poly(acrylic acid-co-acrylamide) and salts
14. Poly(acrylic acid-co-styrene sulfonic acid) and salts
15. Poly(vinyl phosphoric acid)
16. Poly(chloroacrylic acid) and salts
- 25 17. Poly(bromoacrylic acid) and salts
18. Poly(vinyl benzoic acid) and salts
19. Poly(vinyl butyl sulfonic acid) and salts
20. Terpolymers containing acrylamide, acrylic acid and monomer with a general formula:



- 30 Where R_1 = Hydrogen, or alkyl group represented by $-\text{C}_n\text{H}_{(2n+1)}$
 R_2 = Hydrogen, methyl or hydroxy alkyl represented
 by



where $n = 0-6$

and $a =$ at least 1

R_3 = hydrogen or hydroxy alkyl species

21. Terpolymers derived from acrylamide,
5 N-vinyl-2-pyrrolidone and either vinyl acetate or vinyl
pyridine or styrene or methylmethacrylate
22. Quaternized halomethylated poly(2,6-dimethyl-p-phenylene
oxide)
23. Quaternized halomethylated polysulfone
10 24. Quaternized halomethylated poly(p-phenylene
ether-sulfone)

Some of the above listed compounds can be grouped together:

- I. polyacrylamides and substituted
polyacrylamides, partially hydrolyzed (items 1,
15 11, 20)
II. hydroxy containing acrylates (items 2, 3)
III. homopolymers and copolymers of polyacrylic
acid, polystyrene, substituted polyacrylic acid,
and substituted polystyrene, linear and
20 crosslinked (items 5, 6, 12, 13, 14, 16, 17)
IV. cellulosic polymers (items 8, 9, 10)

Most of the polymers listed are either water
soluble or become water soluble on hydrolysis of select
functional groups. These polymers are rendered hydrophilic
25 and water insoluble by one or a combination of the following
techniques: 1) Controlling water soluble portion of the
monomer in a given co- or ter-polymer; 2) Controlling the
degree of hydrolysis of a polymer or a copolymer; and 3)
Introducing optimum crosslinks by incorporating appropriate
30 amounts of crosslinking agents so as to make the polymer
water insoluble but still leave substantial amounts of
hydrophilic groups such as -OH, -COOH, etc. available for
hydrogen bonding type interactions with water.

Figure 1 is a schematic diagram of a fiber optic
35 (subset of an optical waveguide). The key elements are the
core/waveguide 10 and the clad 22 with refractive indices N_1
and N_2 , respectively. The light enters the core 10 at up to
the maximum acceptance angle A_m . Since the light is in a

medium of a different refractive index (N_0 , N_w or N_{wv}) than the core/waveguide (N_1) 10, it is bent (refracted) entering the core 10 and the angle at which it enters the clad 22 is θ_c . Angle θ_c remains a constant as light passes through the
5 fiber by total internal reflection. The light is then refracted again as it passes out of the core 10 into the surrounding medium N_0 , N_w or N_{wv} .

Figure 2 is a schematic diagram of an evanescent wave sensor. In this case, the clad 22 (N_2) has been
10 replaced by the sensing chemistry 12 (N_3). The behavior is similar to that shown in Figure 1 except that the total internal reflection angle θ_c may be different depending on the relationship between N_1 , the refractive index of the core and N_3 , the refractive index of the sensing chemistry.
15 If the sensing chemistry 12 is a thin film, however, which is usually the case for an evanescent wave sensor, then the surrounding medium (N_0 , N_w or N_{wv}) can change the angle θ_c and the light propagation through the fiber is altered. This is not acceptable for a sensor and the present invention
20 obviates this problem.

Figure 3 shows the "sandwich" sensor which is a preferred design and very amenable to the present invention. In this design, there are two objectives: (1) Make optimum use of the sensing chemistry and (2) Minimize or completely
25 eliminate the influence of the background medium. In this arrangement, a minimum of four different refractive indices must be accounted for: (1) N_0 , N_w , or N_{wv} (the refractive index of the surrounding medium), (2) N_1 (the refractive index of the core/waveguide 10), (3) N_2 (the refractive
30 index of the hydrophilic material/clad 22 which is formed of hydrophilic coating 14), and (4) N_3 (the refractive index of the chemistry 12). The key relationship is that N_3 is greater than both N_1 and N_2 . The light enters the core/waveguide 10 at angles up to A_m from medium N_0 , N_w , or
35 N_{wv} . The light is bent (refracted) because N_0 , N_w , or N_{wv} has a different refractive index than the core/waveguide 10(N_1). Since N_3 is greater than N_2 , the light passes

through N_3 and is reflected by N_2 . In the same way, since N_3 is greater than N_1 , it is also reflected by N_1 after the light passes back through N_3 . The light, therefore, gets trapped in chemistry 12 and makes several passes through the chemistry before exiting the sensor. The number of passes, and thus the sensitivity, depends on the relationships between N_3 and N_2 and N_3 and N_1 . In this invention, N_2 (the hydrophilic coating 14) is the important consideration. In U.S. Patent 4,846,548, Klainer presents a "sandwich" sensor with N_2 being a porous clad 22.

According to the invention, clad 22 is replaced (or formed) by hydrophilic coating 14 which can still function as the clad, although not necessarily so, in addition to eliminating light transmission effect due to refractive index differences from the outside media (Figures 4a-g). Thus, hydrophilic coating 14 is: (1) sufficiently porous or of the proper chemical composition to let the analyte reach the chemistry and (2) retains sufficient water so that the sensor always behaves as if it is in a water environment. If coating 14 does not function as the clad e.g. improper refractive index, then an additional cladding layer can be added.

The basic configurations for optical waveguide chemical sensors are shown in Figures 4a through 4g. If the sensing chemistry layer 12 is not present, then the figures are appropriate for optical waveguide sensors with only a single layer on the core 10, e.g., as in Fig. 2. The chemistry could be contained in coating layer 14.

For clarity purposes, the terms "attached" and "immobilized" are defined. Attached refers to chemical configurations where the sensing chemistry, hydrophilic coating, buffer, catalyst, etc. are mechanically bound to each other. The individual compounds that compose the sensor can be painted, sprayed, vaporized, sputtered or evaporated from solution onto a substrate which in this case is waveguide 10. Immobilized indicates that a chemical bond exists between some or all of the chemistries that make up the sensor. Immobilization results in a more stable

sensor than attachment, but often retards or inhibits the sensing mechanism. It is also necessary to define waveguide as a general term of which waveguides, channeled waveguides, single and multi-mode fiber optics and optical "chips" are
5 subsets.

Figure 4a shows a waveguide chemical sensor with sensing chemistry 12 attached to waveguide 10 and hydrophilic coating 14 attached to chemistry 12. This configuration is chosen when the analyte is amenable to
10 transport through coating 14. In this configuration, coating 14 can also act as a protective coating for chemistry 12. In order for this configuration to work, the refractive index of the waveguide, N_1 is less than the refractive index of the chemistry, N_3 and the refractive
15 index of the hydrophilic coating, N_2 must be smaller than N_3 . The light will then be trapped in chemistry layer 12. If coating 14 does not have the right index, a porous layer of suitable index may be formed on coating 14.

Figure 4b shows the waveguide chemical sensor with
20 the hydrophilic coating 14 attached to waveguide 10 and chemistry 12 attached on top of coating 14. This configuration is designed for detecting analytes which will not penetrate coating 14. In this arrangement, an evanescent wave measurement is most practical because light
25 loss through the chemistry is not acceptable. Thus, N_3 must be less than N_1 and N_2 must be greater than N_1 and N_3 . The light will then be trapped in coating 14.

Figure 4c shows the waveguide chemical sensor using two hydrophilic coatings 14 and 18. This arrangement
30 is especially useful for sensor chemistries which work best in the solvated form. This is accomplished by surrounding the chemistry 12 with hydrophilic coatings 14 and 18. Coatings 14 and 18 cannot be the same hydrophilic compounds because of the refractive index requirements. Thus,
35 hydrophilic coating 18 is attached to waveguide 10. Chemistry 12 is attached to coating 18 and coating 14 is attached to chemistry 12. In this case, the refractive index, N_4 of coating 18 has to be greater than N_1 , N_3 has to

be greater than N_4 and N_2 has to be smaller than N_3 . The light will then be trapped in chemistry layer 12.

Figure 4d is the same as Figure 4a except that the chemistry 12 is immobilized on the waveguide 10 by chemical
5 bonds 16. This makes for a much more rugged and stable sensor but, in select situations, may inhibit the sensing chemical reaction.

Figure 4e is the same as Figure 4a except that the hydrophilic material 14 is immobilized on the chemistry 12
10 by chemical bonds 16. This yields a better attachment of the coating, but because of the covalent bonding, can interfere with the sensing chemistry reaction.

Figure 4f is a composite of Figures 4d,e. This represents a sensor assembly where all of the components are
15 immobilized by chemical bonds 16. Once again, in select applications, the stability of the system, due to chemical bonding, can affect its efficacy as a sensor.

Figure 4g is the same as Figure 4a except that hydrophilic coating 14 has been replaced by another
20 hydrophilic coating 20 of index N_5 . It is intended to show that there is no limit to the number of hydrophilic or modified hydrophilic coatings that can be used. Selection is made based on their compatibility with the sensing chemistry and the target analyte.

25 Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only the scope of the appended claims.

CLAIMS

1. An optical waveguide chemical sensor for detecting an analyte, comprising:
 - an optical waveguide of refractive index N_1 ;
 - a sensing chemistry of refractive index N_3 on the waveguide;
 - a hydrophilic coating of refractive index N_2 on the sensor which maintains the sensor in a substantially constant water environment.
2. The sensor of Claim 1 wherein the hydrophilic coating comprises a hydrophilic polymer.
3. The sensor of Claim 1 wherein the hydrophilic coating is attached to the sensing chemistry and sufficiently porous to pass the analyte and the chemistry is attached to the waveguide.
4. The sensor of Claim 3 wherein N_3 is greater than N_1 , and N_2 is less than N_3 .
5. The sensor of Claim 1 wherein the hydrophilic coating is attached to the waveguide and the chemistry is attached to the hydrophilic coating.
6. The sensor of Claim 5 wherein N_3 is less than N_1 and N_2 is greater than N_1 and N_3 .
7. The sensor of Claim 1 further comprising a second hydrophilic coating of refractive index N_4 attached to the waveguide, and wherein the sensing chemistry is attached to the second hydrophilic coating and the hydrophilic coating of index N_2 is attached to the sensing chemistry.
8. The sensor of Claim 7 wherein N_4 is greater than N_1 , N_3 is greater than N_4 , and N_2 is less than N_3 .
9. The sensor of Claim 3 wherein the chemistry is chemically

bonded to the waveguide.

10. The sensor of Claim 3 wherein the hydrophilic coating is chemically bonded to the sensing chemistry.

11. The sensor of Claim 3 wherein the chemistry is chemically bonded to the waveguide and the hydrophilic coating is chemically bonded to the sensing chemistry.

12. The sensor of Claim 3 further comprising hydrophobic or ionic material incorporated into the hydrophilic coating to facilitate passage of the analyte.

13. The sensor of Claim 1 wherein the hydrophilic coating has been saturated with water.

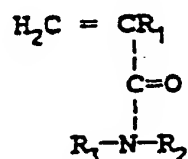
14. The sensor of Claim 1 wherein the hydrophilic coating is selected from the group consisting of:

- a. polyacrylamides and substituted polyacrylamides, partially hydrolyzed
- b. hydroxy containing acrylates
- c. homopolymers and copolymers of polyacrylic acid, polystyrene, substituted polyacrylic acid, and substituted polystyrene, linear and crosslinked
- d. cellulosic polymers.

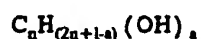
15. The sensor of Claim 1 wherein the hydrophilic coating is selected from the group consisting of:

- a. Poly(acrylamide), hydrolyzed to different degrees and crosslinked, and alkali metal and alkaline earth metal salts thereof
- b. Poly(hydroxy methacrylate)
- c. Poly(hydroxy ethacrylate)
- d. Poly(vinyl acetate) hydrolyzed to different degrees and crosslinked
- e. Poly(acrylic acid), crosslinked
- f. Poly(styrene sulfonic acid) and salts thereof
- g. Poly(vinyl alcohol), crosslinked

- h. Partially carboxylated methyl cellulose
- i. Partially esterified cellulose
- j. Cellulose
- k. Poly(n-acrylamidomethyltrimethyl) ammonium chloride
- l. Poly(acrylic acid-co-styrene)
- m. Poly(acrylic acid-co-acrylamide) and salts thereof
- n. Poly(acrylic acid-co-styrene sulfonic acid) and salts thereof
- o. Poly(vinyl phosphoric acid)
- p. Poly(chloroacrylic acid) and salts thereof
- q. Poly(bromoacrylic acid) and salts thereof
- r. Poly(vinyl benzoic acid) and salts thereof
- s. Poly(vinyl butyl sulfonic acid) and salts thereof
- t. Terpolymers containing acrylamide, acrylic acid and monomer with a general formula:



Where R_1 = Hydrogen, or alkyl group represented by $-\text{C}_n\text{H}_{(2n+1)}$
 R_2 = Hydrogen, methyl or hydroxy alkyl represented
 by



where $n = 0-6$

and $a =$ at least 1

R_3 = hydrogen or hydroxy alkyl species

- u. Terpolymers derived from acrylamide, N-vinyl-2-pyrrolidone and either vinyl acetate or vinyl pyridine or styrene or methylmethacrylate
- v. Quaternized halomethylated poly(2,6-dimethyl-p-phenylene oxide)
- w. Quaternized halomethylated polysulfone
- x. Quaternized halomethylated poly(p-phenylene ether-sulfone).

16. A method of eliminating the effects of exposure to water on an optical waveguide chemical sensor, comprising applying

a hydrophilic coating to the sensor to maintain a substantially constant water environment around the sensor.

17. The method of Claim 16 further comprising forming the hydrophilic coating of a hydrophilic polymer.

18. The method of Claim 16 further comprising incorporating hydrophobic or ionic material in the hydrophilic coating.

19. The method of Claim 16 further comprising saturating the hydrophilic coating with water prior to use.

20. The method of Claim 16 further comprising forming the optical waveguide chemical sensor of a waveguide and a sensing chemistry attached thereto.

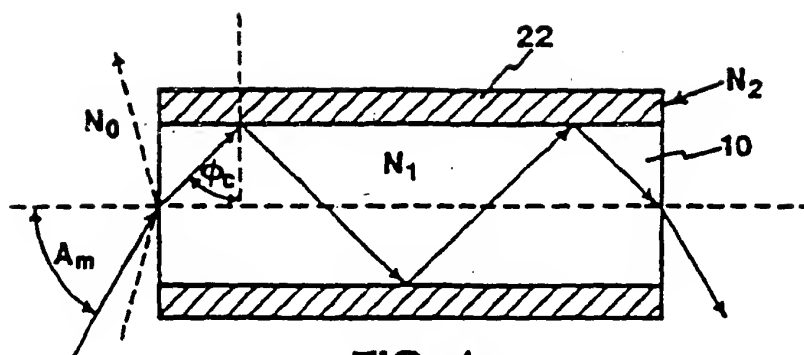


FIG. 1

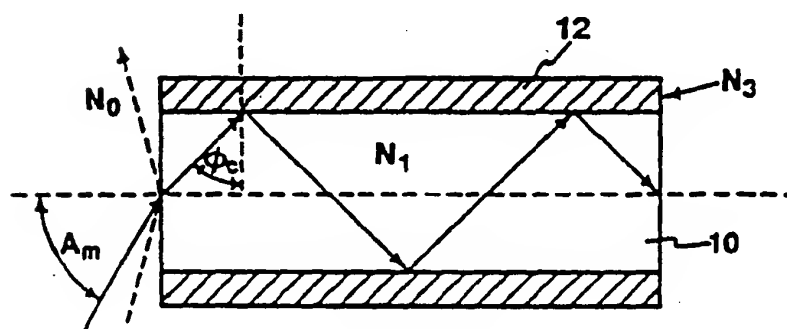


FIG. 2

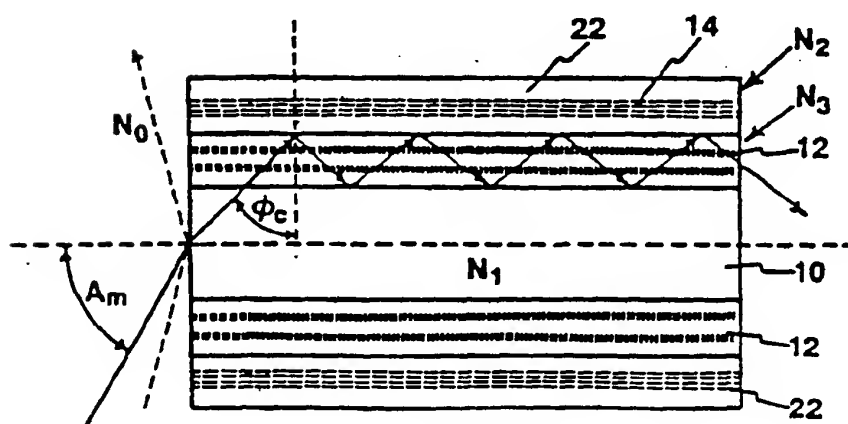


FIG. 3

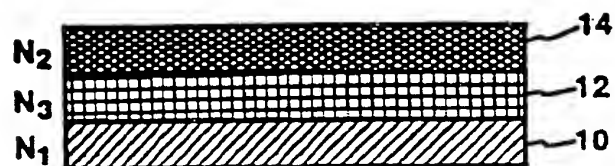


FIG. 4a

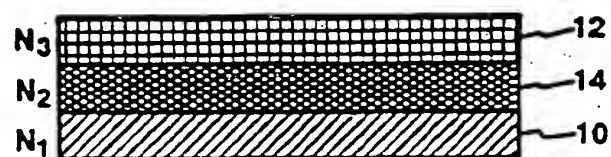


FIG. 4b

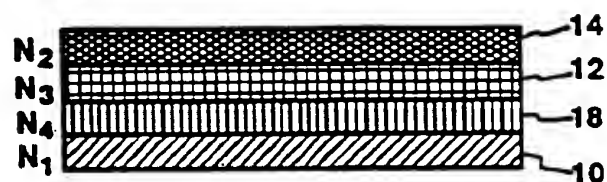


FIG. 4c

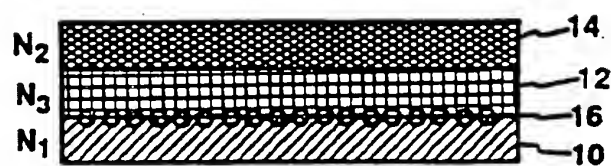


FIG. 4d

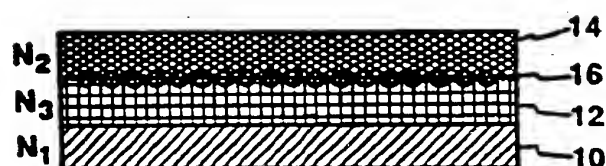


FIG. 4e

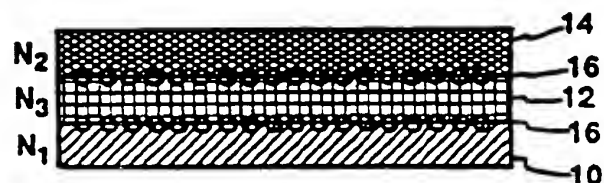


FIG. 4f

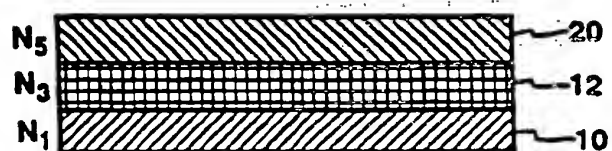
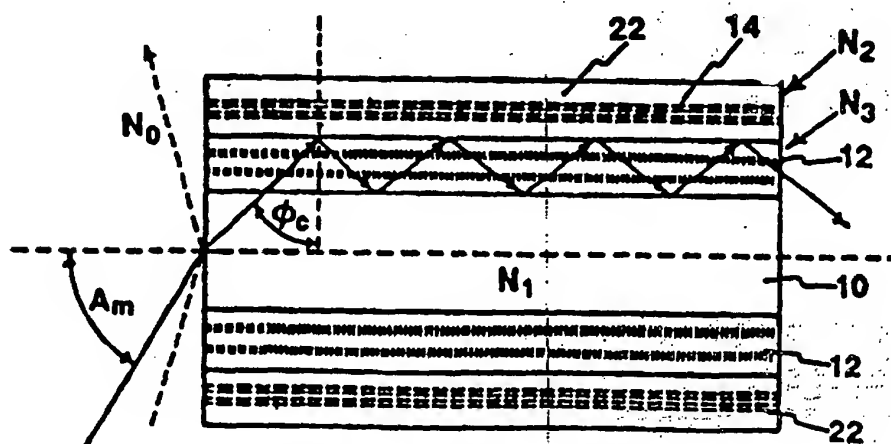


FIG. 4g

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: G01N 21/77, G02B 6/10, 6/16, 6/22, G03C 25/02, G02B 1/04, C09D 201/02	A3	(11) International Publication Number: WO 95/20151 (43) International Publication Date: 27 July 1995 (27.07.95)
(21) International Application Number: PCT/US95/00838 (22) International Filing Date: 19 January 1995 (19.01.95) (30) Priority Data: 181,758 21 January 1994 (21.01.94) US (71) Applicant: FCI-FIBERCHEM, INC. [US/US]; Suite B, 1181 Grier Drive, Las Vegas, NV 89119 (US). (72) Inventors: KLAINER, Stanley, M.; 2063 Sutton Way, Henderson, NV 89014 (US). SOMORJAI, Gabor; 665 San Luis Road, Berkley, CA 94704 (US). DANDGE, Dileep, K.; 17 Reyborn Drive, Henderson, NV 89014 (US). (74) Agents: ABRAHAMS, Colin, P. et al.; Ladas & Parry, 5670 Wilshire Boulevard, Suite 2100, Los Angeles, CA 90036 (US).	(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 17 August 1995 (17.08.95)	

(54) Title: REDUCING THE EFFECTS OF WATER VAPOR AND LIQUID WATER ON OPTICAL WAVEGUIDE SENSORS (OWS) AND OPTICAL WAVEGUIDE CHEMICAL SENSORS (OWCS)

**(57) Abstract**

The effects of water are eliminated from an optical waveguide chemical sensor by applying a hydrophilic coating which creates a pseudo water jacket. The hydrophilic coating absorbs water so that the waveguide sees a constant refractive index. The hydrophilic coating can reach equilibrium conditions in a high relative humidity environment or can be pretreated by exposure to water in a low relative humidity environment. A variety of hydrophilic polymers can be used.

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INTERNATIONAL SEARCH REPORT

National Application No
PCT/US 95/00838

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/77 G02B6/10 G02B6/16 G02B6/22 C03C25/02
G02B1/04 C09D201/02

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 152 287 (J.K.KANE) 6 October 1992 see claims; figures 2-4 ---	1,2,9, 14-17,20
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 49 (P-547) (2496) 14 February 1987 & JP,A,61 217 744 (ORIENT WATCH) see abstract ---	1,5,10, 11,16
A	EP,A,0 481 740 (PURITAN-BENNETT) 22 April 1992 see page 3, line 31 - line 44 see claims; figure 2 ---	1,2,16
A	US,A,5 096 671 (J.A.KANE ET.AL.) 17 March 1992 ---	1,2, 14-16
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A	EP,A,0 244 394 (AVLAG) 4 November 1987 see page 13, line 19 - line 35 see figures 1,2 see page 14, line 1 - line 28 ---	1,9-11
A	DE,A,33 03 941 (LICENTIA) 9 August 1984 see the whole document ---	1,14,15
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 236 (P-601) (2683) 4 August 1987 & JP,A,62 049 242 (NISSHINBO) see abstract ---	1,16
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 215 (P-874) (3563) 19 May 1989 & JP,A,01 032 151 (RICOH) see abstract -----	1,14

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/00838

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5152287	06-10-92	NONE	
EP-A-0481740	22-04-92	JP-A- 5010887	19-01-93
		US-A- 5378432	03-01-95
		US-A- 5277872	11-01-94
US-A-5096671	17-03-92	NONE	
EP-A-0244394	04-11-87	AT-B- 390330	25-04-90
		AT-B- 390678	11-06-90
		DE-A- 3779807	23-07-92
		DK-B- 168414	21-03-94
		JP-B- 6043965	08-06-94
		JP-A- 62261036	13-11-87
		US-A- 5039490	13-08-91
		US-A- 5157262	20-10-92
DE-A-3303941	09-08-84	NONE	

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